(11)

PATENT SPECIFICATION (11) 1 321 275

NO DRAWINGS

1 321 275

(21) Application No. 51165/70 (22) Filed 28 Oct. 1970
(31) Convention Application No. P 19 54 315.8 (32) Filed 29 Oct. 1969 in
(33) Germany (DT)
(44) Complete Specification published 27 June 1973
(51) International Classification C01G 51/02 55/00
(52) Index at acceptance
C1A E10A E10C E2B1 E2RX G28 G9 R
C2C 20Y 229 248 30Y 350 3A13A3A1C 3A13A3B1 3A13A3D 3A13A3J1 408 40Y 54X 66Y TH

(19) THE PATENT OFFICE LONDON

(54) SEPARATION OF METAL CARBONYL CATALYSTS FROM OXO REACTION MIXTURE

(71) We, BADISCHE ANILIN- & SODA-FABRIK AKTIENGESELLSCHAFT, a German joint stock company, of 6700 Ludwigshafen, Federal Republic of Germany, do hereby declare the invention, for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following Statement:—

The invention relates to an improved process for the separation of metal carbonyl catalysts from oxo reaction mixtures by treatment with ion exchangers.

The reaction mixtures obtained from the oxo reaction contain the metal carbonyl complexes used as catalysts in the dissolved state. Since the valuable metals must be recovered and the metal carbonyl compounds contained in the reaction mixture have a detrimental effect on the further treatment of the mixture, these metals must be removed. A number of methods are known for the removal of such metal carbonyl catalysts from oxo reaction mixtures. It is known, for example, to decompose the metal carbonyl catalysts by the action of heat, for example by treating with steam, and thus to recover the metals as such. The recovery of the metals, however, is difficult, since they separate out in a finely divided form which is difficult to isolate and also tend to form metallic "silvering" on the surface of the equipment used. In another method the metal carbonyl catalysts contained in the oxo reaction mixture are decomposed by an oxidizing treatment, for example using air, and the resulting aqueous solution of metal salts is separated from the oxo reaction mixture. This process suffers from the drawback that the oxidizing also attacks the sensitive aldehydes present in the mixture and, furthermore, it does not ensure that the total amount of metal is removed. For this reason it has been proposed to treat the oxo reaction mixture with ion exchangers after it has been subjected to the oxidizing treatment, in order to separate the metal cations. This process has the disadvantage, however, that it is still necessary to carry out an oxidizing treatment of the oxo reaction mixture containing the metal carbonyl catalysts.

The problem to be solved, therefore, is to devise a method of separating the metal carbonyl catalysts from the oxo reaction mixture without the necessity of a prior treatment of the oxo reaction mixture.

We have now found that a metal carbonyl catalyst capable of forming carbonylate anions may be removed more efficiently than hitherto from an oxo reaction mixture by the treatment with an ion exchanger if the crude oxo reaction mixture, containing hydrogen and carbon monoxide, is treated with a basic ion exchanger at a temperature ranging from 0° to 120°C and a pressure ranging from 5 to 700 atmospheres, such that a metal carbonyl hydride is present in the mixture treated with the exchanger.

The novel process has the advantage that the metals may be isolated up to the limit of analytical detectability and, furthermore, they may be removed from the oxo reaction mixture without the formation of metallic "silvering". In addition, the separation, of the metal need not be preceded by a treatment with oxidizing agents which would be detrimental to the oxo reaction mixture.

The preferred oxo reaction mixtures which are used are produced by the reaction of aliphatic, cycloaliphatic or araliphatic olefinically unsaturated compounds of up to 20 carbon atoms and optionally containing a plurality of double bonds, for example two non-conjugated double bonds, or substituents which are inert under the conditions of the reaction, such as alkoxy groups of from 1 to 4 carbon atoms or acyloxy groups, in particular olefins of from 2 to

20 carbon atoms with a mixture of carbon monoxide and hydrogen at temperatures ranging from 80° to 220°C and pressures ranging from 5 to 700 atmospheres, in the presence of metal carbonyl catalysts capable of forming carbonylate anions, preferably those contained in Group VIII of the Periodic Table. The oxo reaction mixtures mainly contain aldehydes and/or alcohols according to the starting materials used. The concentration of the metal carbonyl catalysts is generally from 10 ppm to 1% by weight based on the oxo reaction mixture and calculated as metal.

The crude oxo reaction mixture, containing carbon monoxide and hydrogen, is treated with the basic ion exchanger at temperatures ranging from 0° to 120°C, especially from 20° to 60°C, and at pressures ranging from 5 to 700 atmospheres, especially at pressures ranging from 20 to 300 atmospheres. The pressure and temperature are selected so that the metal carbonyl catalysts are present in the oxo reaction mixture in the form of metal carbonyl hydrides, that is, at lower pressures the temperature must also be lowered accordingly.

The present process has been found to be particularly useful for the removal of cobalt and rhodium carbonyl catalysts, particularly rhodium carbonyl catalysts.

Preferred ion exchanger resins are those containing primary, secondary, tertiary and quaternary amino groups. Of particular interest are ion exchanger resins based on polystyrene and containing tertiary amino groups or quaternary amino groups in the basic form, i.e. with hydroxy cations rather than in self form. Particularly suitable are weakly to strongly basic ion exchangers, for example, "Amberlite" IR 45 and "Dowex" 4. Of particular commercial interest are macroreticular types such as "Amberlyst" A 21, "Lewatit" MP 62, "Lewatit" MP 64, "Imac" A 20, "Zerolit" G, "Amberlite" IRA 93 and "Amberlyst" A26. ("Amberlite", "Amberlyst", "Dowex", "Lewatit." and "Zerolit" are Registered Trade Marks.)

The treatment of the crude oxo reaction mixture with the basic ion exchanger may be effected batchwise, but more preferably it is carried out continuously, for example in a so-called exchanger zone. We have found it advantageous to keep the ratio of length to diameter in the exchanger zone between 5:1 to 50:1. In general the throughput of oxo reaction mixture per kg of basic ion exchanger is from 0.1 to 10 kg per hour.

The process of the present invention is carried out, for example, by producing an oxo reaction mixture in known manner and then immediately passing the resulting oxo reaction mixture without further treatment through an exchanger zone in which any of the specified basic ion exchangers are located, at the specified temperatures and pressures. We prefer to use oxo reaction mixtures in which the starting olefin has been converted to a degree of at least 80%, more preferably of up to more than 90%, to oxo reaction products. The effluent oxo reaction mixture from which the metal carbonyl catalyst has been removed contains only a few ppm of catalyst metal. It can thus be worked up without further treatment in the usual manner, for example by fractional distillation.

The process of the invention is further illustrated in the following Examples.

EXAMPLE 1

Two high-pressure tubes are connected in cascade fashion, the first tube having a length of 500 mm and an inside diameter of 30 mm and being charged with 120 g of "Amberlyst" A 21, whilst the second has a length of 500 mm and an inside diameter of 45 mm and is charged with 222 g of "Amberlyst" A 21. 90 g/h of an oxo reaction product are passed upwardly through the two tubes in succession, which oxo reaction product has been produced by reaction of octene-1 with a mixture of carbon monoxide and hydrogen in equal proportions by volume in the presence of rhodium carbonyl at a temperature of 120°C and a pressure of 280 atmospheres gauge, the said reaction product containing more than 80% by weight of C_9 aldehydes and 20 ppm of rhodium calculated as metal. In the high pressure tube the temperature is kept at from 20 to 30°C and the pressure at 280 atmospheres gauge. The purified oxo reaction mixture has rhodium content of less than 0.1 ppm.

EXAMPLE 2

Example 1 repeated except that only the first high-pressure tube is used and through this there is passed the oxo reaction mixture mentioned in Example 1 and containing rhodium at a concentration of 20 ppm. The oxo reaction mixture purified in this manner contains 0.3 ppm of rhodium.

EXAMPLE 3

Example 1 is repeated except that only the first high-pressure tube is used and this is charged with an oxo reaction mixture similar to that used in Example 1 but having a rhodium content of 40 ppm. After the treatment the oxo reaction mixture contains rhodium at a concentration of 0.6 ppm.

EXAMPLE 4

Example 3 is repeated except that an oxo reaction mixture is used which is obtained by the hydroformylation of octene-1 at 80°C and which contains 80% by weight of C_9 aldehydes. The purified oxo reaction mixture contains 3 ppm of rhodium.

EXAMPLE 5

Example 2 is repeated except that an oxo reaction mixture is used which is obtained by reacting isomeric octenes at 150°C and a pressure of 280 atmospheres with a gas mixture of equal parts by volume of carbon monoxide and hydrogen in the presence of rhodium carbonyl as catalyst. Before purification the oxo reaction mixture contains 20 ppm of rhodium in the form of rhodium carbonyl. After purification the oxo reaction mixture contains 0.1 ppm of rhodium.

EXAMPLE 6

An oxo reaction mixture obtained by reacting vinyl glycol diacetate with a gas mixture of equal parts by volume of carbon monoxide and hydrogen at 110°C and under a pressure of 280 atmospheres in the presence of 40 ppm or rhodium in the form of rhodium carbonyl is passed at a rate of 100 cm^3 per hour through an exchanger tube having a length of 500 mm and an inside diameter of 45 mm and charged with 220 g of "Amberlyst" A 21, the pressure in the tube being 280 atmospheres gauge and the temperature 20-30°C. The purified oxo reaction mixture contains 3 ppm of rhodium.

EXAMPLE 7

An oxo reaction mixture obtained by reacting octene-1 with a gas mixture of equal parts by volume of carbon monoxide and hydrogen at 160°C and 280 atmospheres gauge in the presence of 20 ppm of rhodium as rhodium carbonyl is passed at a rate of 100 cm^3 per hour through an exchanger tube having a length of 500 mm and an inside diameter of 10 mm and charged with 20 g of "Amberlyst" A 21. The quantitatively converted oxo reaction mixture contains, after purification, less than 1 ppm of rhodium.

EXAMPLE 8

Example 2 is repeated except that the crude oxo reaction mixture is treated at a temperature of 60°C. The thus purified oxo reaction mixture contains rhodium at a concentration of 0.1 ppm.

Equally good results are obtained when the treatment is carried out at a temperature of 120°C.

EXAMPLE 9

An oxo reaction mixture obtained by reacting octene-1 with a gas mixture of equal parts by volume of carbon monoxide and hydrogen at 140°C and under a pressure of 280 atmospheres gauge in the presense of 0.09% by weight of cobalt as cobalt carbonyl is passed at a rate of 90 g per hour through an exchanger tube having a length of 500 mm and an inside diameter of 30 mm and charged with "Amberlyst" A 21, the pressure in the tube being 280 atmospheres gauge and the temeprature 60°C. The purified oxo reaction mixture contains 0.001 to 0.003% by weight of cobalt.

If the purification is carried out at 120°C the purified oxo reactio nmixture contains less than 0.001% by weight of cobalt.

EXAMPLE 10

Example 9 is repeated except that the basic ion exchanger resin used is "Lewatit" MP 62. The oxo reaction mixture purified at 60°C contains 0.006% by weight of cobalt, and the oxo reaction mixture purified at 120°C contains 0.001% by weight of cobalt.

WHAT WE CLAIM IS:—

1. A process for the separation of a metal carbonyl catalyst capable of forming carbonylate anions from an oxo reaction mixture using an ion exchanger, wherein the the crude oxo reaction mixture, containing hydrogen and carbon monoxide, is treated with a basic ion exchanger at a temperature ranging from 0° to 120°C and a pressure ranging from 5 to 700 atmospheres such that a metal carbonyl hydride is present in the mixture treated with the exchanger.

2. A process as claimed in claim 1 wherein the oxo reaction mixture contains a cobalt or rhodium carbonyl catalyst.

3. A process as claimed in claim 1 or 2 wherein the ion exchanger contains primary, secondary, tertiary or quaternary amino groups.

4. A process as claimed in claim 3 wherein an ion exchanger resin based on polystyrene and containing tertiary amino groups or quaternary amino groups in the basic form is used.

5. A process as claimed in any of claims 1 to 4, wherein the ion exchanger resin is located in an exchanger zone which has a length to diameter ratio of from 5:1 to 50:1.

6. A process as claimed in any of claims 1 to 5 wherein the throughput of oxo reaction mixture per kg of ion exchanger resin is from 0.1 to 10 kg per hour.

7. A process as claimed in any of claims 1 to 6 wherein a temperature of from 20° to 60°C and a pressure of from 20 to 300 atmospheres are used.

8. A process as claimed in any of claims 1 to 7 wherein the oxo reaction mixture has been produced by reaction of an olefin of from 2 to 20 carbon atoms with a mixture of carbon monoxide and hydrogen at 80 to 220°C and 5 to 700 atmospheres in the presence of a metal carbonyl catalyst capable of forming carbonylate anions so as to convert at least 80% of the olefin to oxo reaction products.

9. A process for the separation of a metal carbonyl catalyst from an oxo reaction mixture substantially as described in any of the foregoing Examples.

10. A hydroformylation process in which the crude oxo reaction mixture produced is subjected to a process as claimed in any of claims 1 to 9 to separate metal carbonyl catalyst therefrom.

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Printed for Her Majesty's Stationery Office by The Tweeddale Press Ltd., Berwick-upon-Tweed, 1973.
Published at the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.